


## Verification of Translation

I, Shuji Yoshizaki, hereby verify that I am familiar with Japanese and English. The attachment is a true English translation of JP 2000-243392.

  
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Date

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Title of the Invention: Positive electrode active material, method for preparing the same,  
and lithium ion secondary battery using the positive electrode  
active material

[Abstract]

[Objectives] The objectives are to effectively use a ferrite, and by using the ferrite, to produce a lithium ion secondary battery having a good properties as well as at an easy rate.

[Solutions]

The objectives are solved by prepared by the steps of: preparing a mixed solution, by mixing a solution obtained by dissolving a complex oxide as shown by a formula of

AFe<sub>2</sub>O<sub>4</sub> (wherein "A" represents Mn, Fe, Zn, Co, Ni or Cr) as a major component, with a first inorganic salt including lithium ion, a second inorganic salt including at least a transition metal element selected from the group consisting of Co, Ni, Mn and Fe, and a complexing agent to form a complex of lithium and the first metal element, wherein the mixed solution is prepared to have a ratio of (lithium ion) : (the ion of the transition metal element) = 1:x ( $0.5 \leq x \leq 1.0$ ); removing a solvent included in the mixed solution by spray-drying to obtain a precursor; and subjecting the precursor to a heat treatment.

[Claim 1] A method for preparation of a positive active material, comprising:

preparing a mixed solution, by mixing a solution obtained by dissolving a complex oxide as shown by a formula of  $AFe_2O_4$  (wherein "A" represents Mn, Fe, Zn, Co, Ni or Cr) as a major component, with a first inorganic salt including lithium ion, a second inorganic salt including at least a first metal element selected from the group consisting of Co, Ni, Mn and Fe, and a complexing agent to form a complex of lithium and the first metal element, wherein the mixed solution is prepared to have a ratio of (lithium ion) : (the ion of the first metal element) = 1:x ( $0.5 \leq x \leq 1.0$ );

removing a solvent included in the mixed solution by spray-drying to obtain a precursor; and

subjecting the precursor to a heat treatment.

[Claim 2] A method for preparation of a positive active material according to claim 1, wherein the first inorganic salt including the lithium ion is selected from the group consisting of lithium nitrate, lithium sulfate, lithium chloride, lithium fluoride, lithium acetate and lithium hydroxide.

[Claim 3] A method for preparation of a positive active material according to claim 1 or claim 2, wherein the second inorganic salt including the first metal element is selected from the group consisting of nitrate, sulfate, chloride, acetate, fluoride and hydroxide.

[Claim 4] A method for preparation of a positive active material according to any of claim 1 to 3, wherein the complexing agent is selected from the group consisting of oxalic acid, tartaric acid, citric acid, succinic acid, malonic acid and maleic acid.

[Claim 5] A positive active material prepared by the method as recited in any of claims 1 to 4, wherein the positive active material has a principle component shown by the

following general formula:  $\text{LiM}_x\text{O}_2$  (wherein "M" represents Co, nickel, Mn, or Fe, satisfying  $0.5 \leq x \leq 1.0$ ).

[Claim 6] A positive active material prepared by the method as recited in any of claims 1 to 4, wherein a complex oxide, whose principle component is of  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$ , is used.

[Claim 7] A positive active material prepared by the method as recited in any of claims 1 to 4, wherein a complex oxide, whose principle component is of  $\text{MnFe}_2\text{O}_4$ , is used.

[Claim 8] A lithium-ion secondary battery comprising: a positive active material layer; a negative active material layer; and a separator holding a non-aqueous electrolyte, provided between the positive active material layer and the negative active material layer, characterized in that the positive active material layer has the positive active material as recited in any of claims 5 to 7.

#### [Detailed Description of the Invention]

[0001]

#### [Field of the Invention]

The present invention relates to a positive active material used in a secondary lithium ion battery, which includes a non-aqueous liquid as an electrolyte, a method for preparing the same, and a lithium ion secondary battery using the same.

[0002]

#### [Description of the Prior Art]

Recently, miniaturization of portable phones and handsets has been developed, and batteries used in such equipments have been demanded to have a higher voltage and

a higher capacity. So, a lithium ion secondary battery, having a non-aqueous liquid as an electrolyte, has been focused on because it has a large output capacity per a unit weight and, therefore, has been under development in various applications.

[0003]

As the positive active material of the lithium ion secondary battery, a layer compound is used, which is capable of electrochemical intercalation of lithium. Such active material has a general formula of  $\text{Li}_y\alpha\text{O}_2$  ( $0.5 \leq y \leq 1.0$ ), and specifically  $\text{Li}\alpha\text{O}_2$ , or a general formula of  $\text{Li}_y\alpha_2\text{O}_2$  (wherein  $\alpha$  represents a transition metal), that is a complex oxide of lithium and a transition metal, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiFeO}_2$  and  $\text{LiMn}_2\text{O}_4$ .

[0004]

As disclosed in U.S. Patent Nos. 4,302,518 and 4,980,080, the complex oxide as mentioned above is generally obtained by: mixing a lithium compound, such as lithium carbonate and lithium oxide, with a transition metal oxide, such as nickel oxide, cobalt oxide and manganese dioxide, and a compound such as a hydroxide, at a predetermined ratio; and baking the mixture at a temperature of 700 to 900 °C for a period of one to several hours in the atmosphere or oxygen.

[0005]

Also, for the purpose of improving, e.g., capacity and/or charge-discharge cycle property, there has been disclosed  $\text{LiNi}_z\text{Co}_{1-z}\text{O}_2$ , which is one combining the complex oxides, as disclosed in JP laid open patent publication No. 63-299056, or one including Al and Ti at a minute amount, as disclosed in JP laid open patent publication No. 5-242891. As such, there are so many proposals as minute amount elements to be added.

[0006]

However, among the active materials, only  $\text{LiCoO}_2$  currently has been practically available, because it produces comparatively high capacity, but there is far cry from its theoretical capacity, bearing improvements

[0007]

The active material is obtained by: mixing a lithium compound, such as lithium carbonate, lithium oxide and lithium hydroxide, with a cobalt compound, such as cobalt oxide and cobalt hydroxide, in a dry process; and baking the mixture at an elevated temperature of  $900^\circ\text{C}$ , approximately. Since such complex oxide is one which is comparatively easy in synthesis, it may be usually synthesized in a general dry process manner, but the dry process limits homogenous mixing. In particular, it is difficult to homogeneously mix a lithium compound having a relatively low gravity with a transition metal having a relatively high gravity by means of the dry process. The heterogeneousness of the mixed powder results in the uniformity or imperfectness of the crystal of the active material, which also results in disturbing migration of the lithium ions in the layer compound of the active material, so as to decrease the battery capacity. Also, the portion where there exist such disorders has an unstable layer structure and is weak in bounding strength between layers, so that the layer structure is broken as repeating intercalation of lithium ions, causing deterioration of the repeating property in the charging and discharging operation. In view of the above, the complex oxides, as obtained by any of the conventional preparation methods, are far from their theoretical capacities, bearing improvements.

[0008]

Then, in order to carry out homogenous mixing of elements composing of an active material, a wet process, that performs mixtures in ion states, has been proposed, which is carried out by dissolving a salt of a lithium compound and a salt of a transition metal compound into water to obtain an aqueous solution. For example, as disclosed I JP patent publications Nos. 5-325966 and 6-44970, salts of, e.g., nickel and lithium, are dissolved in an appropriate solvent, and then mixed in, so-called, a wet manner, followed by balking the mixture to obtain an active material.

[0009]

In these examples, lithium and the transition metal are mixed in ion states and, therefore, they are very homogenously mixed in the aqueous solution. However, the homogenous condition cannot be maintained after removing the solvent such as water, because of forming a segregated salt together with co-existing anions, resulting in drawbacks that each components exist separately and that a targeted homogenous precursor are so difficult to be obtained.

[0010]

In order to solve such drawbacks, a coprecipitation method, in which an appropriate precipitating agent is added to prepare a coprecipitation salt of several ions, and a complex polymerization method, in which a complexing agent is added, which forms a complex compound with the cations in the solution to obtain a precursor have, been considered. By such ways, both cations, that is, lithium ion and a transition metal ion, form a coprecipitation state or a composite complex, and as a result, the homogeneity of the ion mixture in the precursor state has been known to be maintained. For example, JP laid open patent publication No. 6-203834 discloses a method to add ethylene glycol



into lithium and an acetate of a transition metal to form a composite alcoholate, followed by making gelation, which is then baked to obtain an active material. JP laid open patent publication Nos. 6-163046 and 7-142065 disclose a method to make gelation of a salt of a lithium compound and a salt of transition metal compound in a citric acid aqueous solution, which is then baked to obtain an active material.

[0011]

However, regarding the former coprecipitation method, it is difficult in view of principle to coprecipitate elements, that is, alkaline metal ion and transition metal ion, because their chemical properties are significantly different from each other, so that precipitation would occur separately, and thus, this method is difficult to attain the homogeneity of the resultant precipitate.

[0012]

A considerable drawback in the latter complex polymerization method is the means for removing the solvent from the composite complex. Use of various complex agent results in a complex ion forming of several element ions, but such state cannot be always maintained at the time of removing the solvent, and eventually, a precursor would be usually poor in homogeneity, resulting in no difference from that produced by means of the dry process. In case of the reaction between ethylene glycol and citric acid, the solvent is removed little by little, which promotes a condensation reaction, but it needs so long time for the reaction. A gel, once generated, may be re-dissolved by not-removed water or moisture in the atmosphere, to form a salt with coexisting anions, such as acetate ion and nitrate ion, and to be deposited, so that resultant composition is biased, resulting in losing the homogeneity, that is the very same attained by the complex. In the

synthesis of an active material, which absolutely hates water, the wet processes are not appropriate because of the possibility of staying behind water at the stage of the precursor. Further, such processes may always accompany with gelation reaction, so that the resultant precursor is in a state of a sticky gel, being high in hygroscopicity and, resulting in difficulty in handling and involving in problems for treating the gel. Also, these methods necessitate a large amount of the coprecipitating and complexing agent such as ethylene glycol. In addition, because of accompanying a complicated process such as a drying step under a reduced pressure, a yield of the precursor becomes less. Though such methods may be appropriate in powder production for a specialized application, it cannot be a practical production method for the battery application because of consuming a large amount.

[0013]

On the other hand, the spray drying method has been known as another production method for a powder. This method is usually used for the purpose of granulation, but has been reported in the preparation of an active material. For example, the publication {Solid State Ionics 44(1990) pp.87-97} discloses a synthesis method for  $\text{LiNiO}_2$  such that an  $\text{LiOH}$  aqueous solution is mixed with an  $\text{Ni}(\text{OH})_2$  powder to obtain a slurry, which is then subjected to a spray drying, so as to produce a precursor in which the surface of the  $\text{Ni}(\text{OH})_2$  powder is coated with  $\text{LiOH}$ , followed by being baked to obtain an active material. JP laid open patent publication No. 2-9722 discloses a preparation method of spraying an aqueous solution of a manganese compound and a lithium compound by means of a supersonic humidifier, followed by being baked to obtain an active material. However, these methods are used for the purpose of coating

the powder surface and removing the solvent, so that it is not an appropriate way for mass production of an active agent. The precursor obtained only from a solution of raw materials is high hygroscopic, so involving in problems for handling.

[0014]

That is, in order to obtain a highly efficient active material, it would be significantly important to use a wet process superior in homogeneity more than a dry process, as well as to develop a solution composition and solvent removal method, which allows to obtain a precursor which maintains a homogeneously mixed state in the solution having a composition for an active material. Therefore, a spray drying method, combined with a method for obtaining an active material which maintains homogeneity in the ion states, as described in International Application Publication No. WO98/29915, has been found to become superior in handling the precursor, and also, the preparation method using the spray dry method superior also in mass production is found to be most appropriate in production of an active material.

[0015].

[Objectives to be Solved by the Invention]

However, Co, Ni, etc. which are used for these active materials are comparatively expensive metallic elements. In particular, Co is especially expensive and specified as a strategic material, as well as a limited resource, so that it should be a big issue in the future to fully consider its supplying source. In other words, material groups having a composition of  $\beta\text{Fe}_2\text{O}_4$ , wherein “ $\beta$ ” represents a positive ion, which is called as ferrite, are widely used in the field of magnets, magnetic devices, heads for magnetic recording, and magnetic recording mediums. However, despite using an expensive metallic element

such as Co and Ni, together with Fe, as components, used materials are disposed of without careful consideration, and currently are not considered to utilize the waste material.

[0016]

The present invention is made in order to solve these objectives, to obtain a positive active material of a uniform composition, and a method for preparing the same by using a ferrite with good efficiency of mass production. Also, it is also an objective to obtain a lithium ion secondary battery having a superior property using the above positive active material.

[0017]

[Means for Solving the Problem]

The first method for preparation of a positive active material of the present invention comprises: preparing a mixed solution, by mixing a solution obtained by dissolving a complex oxide as shown by a formula of  $AFe_2O_4$  (wherein "A" represents Mn, Fe, Zn, Co, Ni or Cr) as a major component, with a first inorganic salt including lithium ion, a second inorganic salt including at least a first metal element selected from the group consisting of Co, Ni, Mn and Fe, and a complexing agent to form a complex of lithium and the first metal element, wherein the mixed solution is prepared to have a ratio of (lithium ion) : (the ion of the first metal element) = 1:x ( $0.5 \leq x \leq 1.0$ ); removing a solvent included in the mixed solution by spray-drying to obtain a precursor; and subjecting the precursor to a heat treatment.

[0018]

The second method for preparation of a positive active material of the present invention is within the scope of the first method for preparation of a positive active material, and further characterized in that the first inorganic salt including the lithium ion is selected from the group consisting of lithium nitrate, lithium sulfate, lithium chloride, lithium fluoride, lithium acetate and lithium hydroxide.

[0019]

The third method for preparation of a positive active material of the present invention is within the scope of the first or the second method for preparation of a positive active material, and further characterized in that the second inorganic salt including the first metal element is selected from the group consisting of nitrate, sulfate, chloride, acetate, fluoride and hydroxide.

[0020]

The fourth method for preparation of a positive active material of the present invention is within the scope of any of the first, second and third methods for preparation of a positive active material, and further characterized in that the complexing agent is selected from the group consisting of oxalic acid, tartaric acid, citric acid, succinic acid, malonic acid and maleic acid.

[0021]

The first positive active material of the present invention is prepared by the method as mentioned as any of the first, second, third and fourth methods for preparation of a positive active material, and further characterized in that the positive active material has a principle component shown by the following general formula:  $\text{LiM}_x\text{O}_2$  (wherein

“M” represents Co, nickel, Mn, or Fe, satisfying  $0.5 \leq x \leq 1.0$ ).

[0022]

The second positive active material of the present invention is prepared by the method as mentioned as any of the first, second, third and fourth methods for preparation of a positive active material, and further characterized in that a complex oxide, whose principle component is of  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$ , is used.

[0023]

The third positive active material of the present invention is prepared by the method as mentioned as any of the first, second, third and fourth methods for preparation of a positive active material, and further characterized in that a complex oxide, whose principle component is of  $\text{MnFe}_2\text{O}_4$ , is used.

[0024]

The first lithium-ion secondary battery of the present invention comprises: a positive active material layer; a negative active material layer; and a separator holding a non-aqueous electrolyte, provided between the positive active material layer and the negative active material layer, characterized in that the positive active material layer has the positive active material as recited in any of claims 5 to 7.

[0025]

[Embodiment of the Invention]

The method for preparation of a positive active material as the first aspect of the present invention, comprises: preparing a mixed solution, by mixing a solution obtained by dissolving a complex oxide (so-called, ferrite) as shown by a formula of  $\text{AFe}_2\text{O}_4$  (wherein “A” represents Mn, Fe, Zn, Co, Ni or Cr) as a major component, with a first

inorganic salt including lithium ion, a second inorganic salt including at least a first metal element (transition metal) selected from the group consisting of Co, Ni, Mn and Fe, and a complexing agent to form a complex of lithium and the first metal element, wherein the mixed solution is prepared to have a ratio of (lithium ion) : (the ion of the first metal element) = 1:x ( $0.5 \leq x \leq 1.0$ ); removing a solvent included in the mixed solution by spray-drying to obtain a precursor; and subjecting the precursor to a heat treatment. In this case, the "A" of the complex oxide, having the composition of  $AFe_2O_4$ , is Mn, Fe, Zn, Co, Ni or Cr, it may be possible to prepare a positive active material having good properties.

[0026]

Also, as the first inorganic salt including lithium ion, it may possible to use lithium nitrate, lithium sulfate, lithium chloride, lithium fluoride, lithium acetate, or lithium hydroxide.

[0027]

Moreover, the second inorganic salt including the first metal element (transition metal element) is used by selecting from the group consisting of nitrate, sulfate, chloride, acetate, fluoride and hydroxide. In this case, the first metal element is mainly of a transition metal such as Co, Ni, Mn, Fe and so on, which is a composition of an active material, but possible to include another metal in order to improve properties. As the metal element which may be added, it has been variously proposed to include a very small amount of Al, Ti, Mg, Zn, V, Ba, Mg, Sr, Ca, and so on.

[0028]

Moreover, as the complexing agent, it may be preferable to use one having a water solubility and having a hydroxyl group or carboxyl group, which may easily form a

complex with lithium ion and a transition metal ion, and specifically, an organic acid such as oxalic acid, tartaric acid, citric acid, succinic acid, malonic acid and maleic acid may be used. There are some other acids, such as EDTA (ethylenediaminetetraacetic acid) and HEDTA (hydroxy ethylenediamine triacetic acid), as a complexing agent which forms a complex. However, because these acids stay behind a nitride compound in the precursor at the time of heat decomposition, these compounds may involve in problems that is reducing battery property due to crystal disorders.

[0029]

The spray dry method used in the present invention is well known in view of a method superior in mass production compared with a wet process, in the field of, e.g., ceramic powder production, and using this method makes possible to efficiently synthesize an active material precursor at a mass production. Further, after finishing the spray dry method, a precursor can be collected in a state of an organic acid composite complex of lithium and a transition metal, in which water component or solvent is not contained and therefore, it is significantly easy to handle the dried precursor. The spray temperature for the spray drying is at a temperature of 160 to 220°C, and especially, at a temperature of 180 to 200°C. Less than the above temperature range, the precursor is insufficient to be dried so as to hold crystal water and to become significant in hygroscopicity. On the other hand, more than the above temperature range, the formed composite complex may generate heat decomposition without control, resulting in an oxide high in hygroscopicity, again, which does not accomplish the objective to obtain homogenous mixture, nor reduces the yield of the precursor, resulting in much less handling. The spray pressure for the spray dry method is at a pressure of 0.5 to 2.0Pa,



which eventually results in good active material.

[0030]

According to the preparation method of the positive active material of the first aspect of the present invention, a ferrite, which is, e.g., a waste material, is used as a resource for elements such as Co, Ni, Mn and Fe, etc. for making an active material. By dissolving the ferrite followed by producing it into an active material as explained above, a positive active material having good properties could be obtained. Also, it has been newly discovered that Fe that is one of components of the ferrite does not adversely affect in the functions of the active material.

[0031]

In other words, according to the embodiment of the present invention, a ferrite, that had been used as a final oxide product, is used to prepare a dissolving solution, so that it is used as a resource for a part of the components of the active material and, then, a complexing agent forms a composite complex. While the composite complex maintains a homogenous ions mixture state, the solvent is removed in a moment so as to obtain a active material precursor without being adversely affected by water component and solvents inside the precursor, and by moisture in the atmosphere. Baking the precursor makes an active material having a good performance, resulting in accomplishing a battery property with high performance

[0032]

Also, the above mentioned precursor is extremely rich in homogeneity and absent from impurities inside thereof, such as moisture and solvents, so that it is superior in reactivity and, therefore, it may be possible to bake it at a lower temperature by 50 to

150°C than those of a general dry process. Further, lowering the baking temperature prevents a lithium component of an active material from dispersing during the baking. Therefore, an ideal active material, which is in accordance with a stoichiometry, can be obtained, directing it to improvement of the battery properties. However, the baking temperature of an active material depends on the kind of the active material, so that the general temperature is described to be at a temperature of 600 to 850°C, but this description shall not be construed to limit the scope of the present invention.

[0033]

The size of the active material obtained may be arbitrarily controlled by adjusting boiling point of the sprayed solution, temperature for the spraying, atomizing pressure, diameter of a two fluid nozzle, etc. However, this description here shall not be construed to limit the scope of the obtained active material into its shape and particle size, and any active material may be used.

[0034]

#### Second Aspect of the Present Invention

The present invention of the second aspect of the present invention is a positive active material having a principle component shown by the following general formula:  $\text{LiM}_x\text{O}_2$  (wherein "M" represents Co, nickel, Mn, or Fe, satisfying  $0.5 \leq x \leq 1.0$ ), which is prepared by the preparation method as recited in claim 1.

[0035]

Also, within the scope of the first aspect of the present invention, a complex oxide, whose principle component is of  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$ , may be used, so as to obtain a

positive active material having  $\text{Li}(\text{Co},\text{Ni})\text{O}_2$  as a principle component.

[0036]

Also, within the scope of the first aspect of the present invention, a complex oxide, whose principle component is, e.g., of  $\text{MnFe}_2\text{O}_4$ , may be used, so as to obtain a positive active material having  $\text{LiMn}_2\text{O}_2$  as a principle component.

[0037]

Also, within the scope of the first aspect of the present invention, the first metal element forming a composite complex with lithium is in a range of 0.5 to 1.0 by molar ratio per lithium, which makes superiority in positive capacity. Less than 0.5 or more than 1.0 will reduce the capacity.

[0038]

#### Third Aspect of the Present Invention

Fig.1 shows a general block diagram of a lithium ion secondary battery. In the drawing, “1” shows a positive active material layer, “2” shows a positive collector, “3” shows a positive case, “4” shows a gasket of an insulating material, “5” shows a separator holding a non-aqueous electrolyte including lithium ions, “6” shows a negative active material layer, “7” shows a negative collector, and “8” shows a negative case. Namely, it has a separator 5 holding a non-aqueous electrolyte, provided between a positive active material layer 1 and a negative active material 6. In the embodiment of the present invention, the positive active material 1 as explained above has the positive active material as the second embodiment of the present invention.

[0039]

Examples are described in detail as follows:

### Example 1

$\text{CoFe}_2\text{O}_4$  was used as a ferrite, which was dissolved in hydrochloric acid to obtain a solution at a concentration of 0.1M/l. Then, lithium nitrate and cobalt nitrate in powder were dissolved into tartaric acid to obtain a tartaric acid aqueous solution having a concentration of 0.2M/l. These solutions were mixed after weighting each of the volumes, to have a stoichiometric ratio for the active material,  $\text{LiCoO}_2$ . Continuing the stirring for 30 minutes, a spray dry was conducted by means of a spray dryer. Spray of the solution was generated by means of a dual nozzle accompanied with a compressed air, sending the solution at a rate of 100ml per a minute and at a pressure of 2.0MPa. The solution was sprayed at a temperature of 200°C, obtaining a precursor of the active material at a yield of 95% or more.

[0040]

The precursor powder, after dried, was put into a quartz boat, which was then baked at a temperature of 800 °C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder. The active material of this Example obtained in accordance with the present invention was examined by means of an X ray diffraction method to find it to be  $\text{LiCoO}_2$  including Fe.

[0041]

Then, a lithium secondary battery as shown in Fig. 1 was produced using the active material obtained as mentioned above. Inside a glove box under an argon atmosphere, the active material was weighted to be 90wt(s)%, an electric conduction material that is acetylene black having an averaged particle size of 3.0  $\mu\text{m}$  was weighted to be 5wt%, and a binder (binding agent) that is polyvinylidene fluoride (PVDF) was

weighted to be 5wt(s)% and, then, the weighted components were mixed with a solvent that is N-methyl pyrrolidone (NMP), so as to obtain a paste. This paste was coated on an aluminum foil, which was finally to be the positive electrode collector 2, by means of a doctor blade method, followed by drying it in an oven under vacuum at a temperature of 150°C and, then, pressing it to obtain the positive active material layer 1.

[0042]

Metal lithium was used as the negative electrode active material layer 6, which was filled in a negative electrode case 8 together with a negative electrode collector 7. A mixed solution of ethylene carbonate (EC), 1,2-dimethoxyethane (DME) and 1.0M lithium perchlorate was used as an electrolytic solution, which was penetrated into a separator 5 made of polypropylene (PP), followed by holding it between the negative electrode active material layer 6 and the positive active material layer 1, which was then put into a positive electrode case 3 together with the positive electrode collector 2, followed by being closed by a gasket 4, so as to obtain a coin type battery as shown in Fig. 1. This battery is referred to as Sample A.

[0043]

Using this battery, a charge and discharge measurement was made under a constant current mode at a current density of 0.1 mA/cm<sup>2</sup>, whose results obtained are shown in Table 1. In the measurement, the upper limit of the charge voltage was set up to 4.2V.

[0044]

[Table 1]

Example	Comparative Example
---------	---------------------

	Discharge Capacity (mAh/g)		Discharge Capacity (mAh/g)			
1	A	167	R1	138	RF1	140
2	B	195	R2	155	RF2	152
3	C	190	R3	168	RF3	167
4	D	140	R4	124	RF4	125
5	E	191	R5	159	RF5	158
6	F	137	R6	119	RF6	111

[0045]

#### Example 2

NiFe<sub>2</sub>O<sub>4</sub> was used as a ferrite, which was dissolved in hydrochloric acid to obtain a solution at a concentration of 0.1M/l. Then, a citric acid aqueous solution was prepared, which included lithium acetate, nickel acetate and citric acid, each of which had an adjusted concentration of 0.2M. These solutions were mixed after weighting each of the volumes, to have a stoichiometric ratio for the active material, LiNiO<sub>2</sub>. Continuing the stirring for a period of 30 minutes, a spray dry, similar to Example 1, was conducted by means of a spray dryer. Spray of the solution was generated by means of a dual nozzle accompanied with a compressed air, sending the solution at a rate of 100ml per a minute and at a pressure of 1.5MPa. The solution was sprayed at a temperature of 190°C, obtaining a precursor of the active material at a yield of 95% or more.

[0046]

The precursor powder, after dried, was put into a quartz boat, which was then baked at a temperature of 700 °C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder. The active material of the example obtained in accordance with the present invention was examined by means of an X ray diffraction method to find it to be  $\text{LiNiO}_2$  including Fe.

[0047]

Using this active material, a coin type battery, which is referred to as Sample B, was prepared, and a charge and discharge measurement in the same manner as Example 1 was made, whose results obtained are shown in Table 1.

[0048]

#### Example 3

$\text{NiFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  were used as ferrite, which were dissolved in a mixed acid of hydrochloric acid and nitric acid to obtain a solution at a concentration of 0.1M/l. Then, an aqueous solution was prepared which included lithium chloride, cobalt chloride, nickel chloride and oxalic acid, each of which had an adjusted concentration of 0.2M. These solutions were mixed after weighting each of the volumes, to have a stoichiometric ratio for the active material,  $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$ . Continuing the stirring for a period of 30 minutes, a spray dry, similar to Example 1, was conducted by means of a spray dryer. The solution was sprayed at a temperature of 220°C, obtaining a precursor of the active material at a yield of 95% or more.

[0049]

The precursor powder, after dried, was put into a quartz boat, which was then baked at a temperature of 750 °C in the atmosphere for a period of 10 hours, so as to

obtain a dark-brown powder. The active material of this Example obtained in accordance with the present invention was examined by means of an X ray diffraction method to find it to be  $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$  including Fe.

[0050]

Using this active material, a coin type battery was prepared in the same manner as Example 1, which is referred to as Sample C, and a charge and discharge measurement was made in the same manner as Example 1, whose results obtained are shown in Table 1.

[0051]

#### Example 4

A  $\text{MnFe}_2\text{O}_4$  magnet was used as a ferrite, which was set as an anode, while using platinum as a cathode, and electrolysis was carried out in a dilute hydrochloric acid to dissolve the  $\text{MnFe}_2\text{O}_4$  magnet, so as to obtain a solution at a concentration of 0.1M/l. Then, aqueous solutions, each including lithium sulfate, manganese nitrate and malonic acid, and each having an adjusted concentration of 0.2M, were prepared. Then, these solutions were mixed after weighting each of the volumes, to have a stoichiometric ratio for the active material,  $\text{LiMn}_2\text{O}_4$ . Continuing the stirring for a period of 30 minutes, a spray dry, similar to Example 1, was conducted by means of a spray dryer. The solution was sprayed at a temperature of  $180^\circ\text{C}$ , obtaining a precursor of the active material at a yield of 95% or more.

[0052]

The precursor powder, after dried, was put into a quartz boat, which was then baked at a temperature of  $800^\circ\text{C}$  in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder. The active material of this Example obtained in accordance



with the present invention was examined by means of an X ray diffraction method to find it to be  $\text{LiMn}_2\text{O}_4$  including Fe.

[0053]

Using this active material, a coin type battery was prepared in the same manner as Example 1, which is referred to as Sample D, and a charge and discharge measurement was made in the same manner as Example 1, whose results obtained are shown in Table 1.

[0054]

Example 5

$(\text{Ni,Zn})\text{Fe}_2\text{O}_4$  bar was used as a ferrite, which were dissolved in the mixed acid, as used in Example 3, to obtain a solution at a concentration of 0.1M/l. Then, an aqueous solution was prepared including lithium hydroxide which had an adjusted concentration of 0.2M. Then, 0.2M amount nickel hydroxide was dissolved in a citric acid aqueous solution having an adjusted concentration of 0.2M, so as to obtain a citric acid aqueous solution including nickel ions. Thereafter, these solutions were mixed after weighting each of the volumes, to have a stoichiometric ratio for the active material,  $\text{LiNiO}_2$ . Continuing the stirring for a period of 30 minutes, a spray dry, similar to Example 1, was conducted by means of a spray dryer. The solution was sprayed at a temperature of  $210^\circ\text{C}$ , obtaining a precursor of the active material at a yield of 95% or more.

[0055]

The precursor powder, after dried, was put into a quartz boat, which was then baked at a temperature of  $700^\circ\text{C}$  in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder. The active material of the example obtained in accordance

with the present invention was examined by means of an X ray diffraction method to find it to be  $\text{LiNiO}_2$  including Fe and Zn.

[0056]

Using this active material, a coin type battery was prepared in the same manner as Example 1, which is referred to as Sample E, and a charge and discharge measurement was made in the same manner as Example 1, whose results obtained are shown in Table 1.

[0057]

Example 6

$(\text{Mn,Zn})\text{Fe}_2\text{O}_4$  powder was used as a ferrite, which were dissolved in hydrochloric acid to obtain a solution at a concentration of 0.1M/l. Then, a succinic acid aqueous solution was prepared including lithium nitrate, manganese nitrate and succinic acid, each of which had an adjusted concentration of 0.2M. Then, these solutions were mixed after weighting each of the volumes, to have a stoichiometric ratio for the active material,  $\text{LiMn}_2\text{O}_4$ . Continuing the stirring for a period of 30 minutes, a spray dry, similar to Example 1, was conducted by means of a spray dryer. The solution was sprayed at a temperature of  $220^\circ\text{C}$ , obtaining a precursor of the active material at a yield of 95% or more.

[0058]

The precursor powder, after dried, was put into a quartz boat, which was then baked at a temperature of  $800^\circ\text{C}$  in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder. The active material of the example obtained in accordance with the present invention was examined by means of an X ray diffraction method to find

it to be  $\text{LiMn}_2\text{O}_4$  including Fe and Zn.

[0059]

Using this active material, a coin type battery was prepared in the same manner as Example 1, which is referred to as Sample F, and a charge and discharge measurement was made in the same manner as Example 1, whose results obtained are shown in Table 1.

[0060]

#### Comparative Example 1

In accordance with a dry process that is a conventional and most general preparation method, lithium carbonate and cobalt oxide were weighted to show the same stoichiometric ratio of the active material of Example 1, followed by mixing them by using a ball mill for a period of 2 hours. Then, the mixture was put into a quartz boat, which was then baked at a temperature of 900 °C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder, which is referred to as Sample r1.

Meanwhile, in accordance with a conventional another wet process, lithium carbonate and cobalt oxide were added into and mixed with the ferrite solution prepared in Example 1 such that the stoichiometric ratio of the active material would be the same as Example 1, followed by being dried. Then, the mixture was put into a quartz boat, which was then baked at a temperature of 900 °C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder, which is referred to as Sample rf1.

[0061]

Using these active materials (r1, rf1), coin type batteries were prepared in the same manner as Example 1, which are referred to as Samples R1, RF1, and to each of the

samples, a charge and discharge measurement was made in the same manner as Example 1, whose results obtained are shown in Table 1.

[0062]

#### Comparative Example 2

Similar to Comparative Example 1, in accordance with a dry process that is a conventional and most general preparation method, lithium carbonate and nickel hydroxide were weighted to show the stoichiometric ratio of the active material of Example 2, followed by mixing them by using a ball mill for a period of 2 hours. Then, the mixture was put into a quartz boat, which was then baked at a temperature of 800 °C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder, which is referred to as Sample r2. Meanwhile, in accordance with a conventional another wet process, lithium carbonate and nickel hydroxide were added into and mixed with the ferrite solution prepared in Example 2 such that the stoichiometric ratio of the active material would be the same as Example 2, followed by being dried. Then, the mixture was put into a quartz boat, which was then baked at a temperature of 800 °C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder, which is referred to as Sample rf2.

[0063]

Using these active materials (r2, rf2), coin type batteries were made in the same manner as Example 1, which are referred to as Samples R2, RF2, and to each of the samples, a charge and discharge measurement in the same manner was applied, whose results obtained are shown in Table 1.

[0064]

### Comparative Example 3

In accordance with a dry process that is a conventional and most general preparation method, lithium carbonate, nickel hydroxide and cobalt hydroxide were weighted to show the stoichiometric ratio of the active material of Example 3, followed by mixing them by using a ball mill for a period of 2 hours. Then, the mixture was put into a quartz boat, which was then baked at a temperature of 850 °C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder, which is referred to as Sample r3. Meanwhile, in accordance with a conventional another wet process, lithium carbonate, nickel hydroxide and cobalt hydroxide in powder were added into and mixed with the ferrite solution prepared in Example 3 such that the stoichiometric ratio of the active material would be the same as Example 3, followed by being dried. Then, the mixture was put into a quartz boat, which was then baked at a temperature of 850 °C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder, which is referred to as Sample rf3.

[0065]

Using these active materials (r3, rf3), coin type batteries were prepared in the same manner as Example 1, which are referred to as Samples R3, RF3, and to each of the samples, a charge and discharge measurement in the same manner was applied, whose results obtained are shown in Table 1.

[0066]

### Comparative Example 4

Lithium nitrate and manganese nitrate were weighed, which were added and dissolved into an ion-exchanged water weighted such that each of the ions were at a

concentration of 0.2M, so as to obtain a mixture solution having the same stoichiometric ratio as the active material of Example 4 in view of lithium and manganese ions. This solution was heated while stirring it drastically with a magnetic stirrer, for drying off the solvent therein to obtain a precursor. This precursor was collected and dried under vacuum at a temperature of 200°C for a period of 2 hours, which was then put into a quartz boat and baked at a temperature of 850 °C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder, which is referred to as Sample r4. Meanwhile, in accordance with a conventional another wet process, lithium nitrate and manganese nitrate in powder were added into and mixed with the ferrite solution prepared in Example 4 such that the stoichiometric ratio of the active material would be the same as Example 4, followed by being dried, which was put into a quartz boat and baked at a temperature of 850 °C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder, which is referred to as Sample rf4.

[0067]

Using these active materials (r4, rf4), coin type batteries were prepared in the same manner as Example 1, which are referred to as Samples R4, RF4, and to each of the samples, a charge and discharge measurement in the same manner was applied, whose results obtained are shown in Table 1.

[0068]

#### Comparative Example 5

Lithium nitrate and nickel nitrate were weighed, which were added and dissolved into an ion-exchanged water weighted such that each of the ions were at a concentration of 0.2M, so as to obtain a mixture solution having the same stoichiometric ratio as the

active material of Example 5 in view of lithium and nickel ions. Into this solution, a citric acid aqueous solution having an adjusted concentration of 0.2M was further added. Such solution were applied to an rotary evaporator under a reduced pressure of 1000Pa in a hot bath having a temperature of 60°C to dry off the solvent, resulting in making gelation during a period of 48 hours. This gelating material was collected and dried under vacuum at a temperature of 200°C for a period of 2 hours, which was then put into a quartz boat and baked at a temperature of 750°C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder, which is referred to as Sample r5. Meanwhile, in accordance with a conventional another wet process, lithium nitrate and nickel nitrate in powder were added into and mixed with the ferrite solution prepared in Example 5 such that the stoichiometric ratio of the active material would be the same as Example 5, followed by being dried, which was put into a quartz boat and baked at a temperature of 750°C in the atmosphere for a period of 10 hours, so as to obtain dark-brown powder, which is referred to as Sample rf5.

[0069]

Using these active materials (r5, rf5), coin type batteries were prepared in the same manner as Example 1, which are referred to as Samples R5, RF5, and to each of the samples, a charge and discharge measurement in the same manner was applied, whose results obtained are shown in Table 1.

[0070]

#### Comparative Example 6

Lithium acetate and manganese acetate were weighed, which were added and dissolved into an ion-exchanged water weighted such that each of the ions were at a

concentration of 0.2M, so as to obtain a mixture solution having the same stoichiometric ratio as the active material of Example 6 in view of lithium and manganese ions. Into this solution, an ethylene glycol aqueous solution having an adjusted concentration of 0.4M was further added. Such solution were heated with drastically stirring in a hot bath having a temperature of 90°C for drying of the solvent therein, proceeding with polymerization reaction for a period of 24 hours. The resultant was collected and dried under vacuum at a temperature of 150°C for a period of 2 hours, which was then put into a quartz boat and baked at a temperature of 850°C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder, which is referred to as Sample r6. Meanwhile, in accordance with a conventional another wet process, lithium acetate and manganese acetate in powder were added into and mixed with the ferrite solution prepared in Example 6 such that the stoichiometric ratio of the active material would be the same as Example 6, followed by being dried, which was put into a quartz boat and baked at a temperature of 850°C in the atmosphere for a period of 10 hours, so as to obtain a dark-brown powder, which is referred to as Sample rf6.

[0071]

Using these active materials (r6, rf6), coin type batteries were prepared in the same manner as Example 1, which are referred to as Samples R6, RF6, and to each of the samples, a charge and discharge measurement in the same manner was applied, whose results obtained are shown in Table 1.

[0072]

Table 1 shows that each of the positive active materials of Examples 1 to 6 has a higher discharge capacity than any of Comparative Examples. Moreover, inclusion of Fe,



or Fe and Zn is found not to adversely affect the properties of discharge capacity.

[0073]

Furthermore, while “A” of the complex oxide,  $AFe_2O_4$ , is selected from the group consisting of Mn, Fe, Zn, Co, Ni and Cr, the combination other than used in Examples 1 to 6 were selected, researching the discharge capacities in the same manner as Examples 1 to 6 and Comparative Examples 1 to 6. As a result, all of the other examples using the positive active material according to the present invention had a higher discharge capacity than the other comparative examples by 10 to 30mAh/g.

[0074]

[Effects of the Invention]

The first method for preparation of the positive active material of the present invention comprises: preparing a mixed solution, by mixing a solution obtained by dissolving a complex oxide as shown by a formula of  $AFe_2O_4$  (wherein A represents Mn, Fe, Zn, Co, Ni or Cr) as a major component, with a first inorganic salt including lithium ion, a second inorganic salt including at least a first metal element selected from the group consisting of Co, Ni, Mn and Fe, and a complexing agent to form a complex of lithium and the first metal element, wherein the mixed solution is prepared to have a ratio of (lithium ion) : (the ion of the first metal element) = 1:x ( $0.5 \leq x \leq 1.0$ ); removing a solvent included in the mixed solution by spray-drying to obtain a precursor; and subjecting the precursor to a heat treatment, resulting in an effect that use of a ferrite improves easy and good mass production.

[0075]

The second method for preparation of the positive active material of the present invention is within the scope of first method for preparation of the positive active material, and further characterized in that the first inorganic salt including the lithium ion is selected from the group consisting of lithium nitrate, lithium sulfate, lithium chloride, lithium fluoride, lithium acetate and lithium hydroxide, resulting in an effect that use of a ferrite improves easy and good mass production.

[0076]

The third method for preparation of the positive active material is within the scope of the first or the second method for preparation of the positive active material, further characterized in that the second inorganic salt including the transition metal element is selected from the group consisting of nitrate, sulfate, chloride, acetate, fluoride and hydroxide, which results in an effect that use of a ferrite improves easy and good mass production.

[0077]

The fourth method for preparation of the positive active material is within the scope of any of the first to the third methods for preparation of the positive active material, the complexing agent is selected from the group consisting of oxalic acid, tartaric acid, citric acid, succinic acid, malonic acid and maleic acid, which results in an effect that use of a ferrite improves easy and good mass production.

[0078]

The first positive active material of the present invention is prepared by the method as mentioned as any of the first to fourth method for preparation of the positive active material, further characterized in that the positive active material has a principle

component shown by the following general formula:  $\text{LiM}_x\text{O}_2$  (wherein "M" represents Co, nickel, Mn, or Fe, satisfying  $0.5 \leq x \leq 1.0$ ), which results in an effect to obtain an homogenous composition.

[0079]

The second positive active material of the present invention is prepared by the method as mentioned as any of the first to fourth method for preparation of the positive active material, and further characterized in that a complex oxide, whose principle component is of  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$ , is used, which results in an effect to obtain an homogenous composition.

[0080]

The third positive active material of the present invention is prepared by the method as mentioned as any of the first to fourth methods for preparation of the positive active material, and further characterized in that a complex oxide, whose principle component is of  $\text{MnFe}_2\text{O}_4$ , is used, which results in an effect to obtain an homogenous composition.

[0081]

The first lithium-ion secondary battery of the present invention comprises: a positive active material layer; a negative active material layer; and a separator holding a non-aqueous electrolyte, provided between the positive active material layer and the negative active material layer, characterized in that the positive active material layer has the positive active material as mentioned as any of the first to third positive active materials, which results in an effect excellent in properties.

[Brief Description of the Drawing]

[Fig. 1] This drawing shows an illustrative view of a typical coin type battery.

[Description of the Symbols]

1: positive active material layer

2: positive electrode collector

5: separator

6: negative active material layer

7: negative electrode collector